8-1-1970

The Removal of Sodium from Lignite by Ion Exchange

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THE REMOVAL OF SODIUM FROM LIGNITE BY ION EXCHANGE

by

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Bachelor of Science, University of North Dakota 1969

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

August
1970

This thesis submitted by John T. Crystal in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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ACKNOWLEDGEMENTS

The author wishes to express appreciation to the Bureau of Mines Coal Research Laboratory, United States Department of the Interior, at Grand Forks, North Dakota, and the University of North Dakota, Grand Forks, North Dakota, for the fellowship under which this work was done.

The author also wishes to thank Dr. Thomas C. Owens, Dr. Donald E. Severson, and Dean T. J. Clifford for their advice and guidance in this work.

Special acknowledgement is due Messrs. J. J. Hoeppner and E. F. Bitzan for their analyses of the many samples generated by this work.

Appreciation is also extended to Mr. Donald J. Winge for his work on illustrations, Miss Lois J. Voelker for typing this thesis, and the other employees of the Bureau of Mines who assisted in this investigation.

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ABSTRACT

The rate and extent of sodium removal from lignite by ion exchange ere studied using calcium chloride solutions. The experimental apparatus onsisted of a centrifugal stirring device in a limited bath. Four variables, otation speed, calcium chloride concentration, particle size, and moisture ontent were considered.

It was determined that rotation speed had no discernable effect on he rate or extent of sodium removal. Particle size and moisture content, owever, do have considerable effect on the rate and extent of sodium emoved. It was also found that as the calcium chloride concentration as decreased the exchange approached theoretical stoichiometric proportions.

The observed phenomena were found to agree quite well with a hysical model of lignite first postulated by Lavine.

INTRODUCTION

The ever increasing demand for electrical power is well recognized in he United States. North Dakota has large reserves of lignite coal hich represent a potential source of energy to aid in meeting this emand. One of the recognized problems in the use of lignite, however, s its tendency to foul the boiler tube surfaces in the powerplant (1).

It has also been established that the fouling tendency of a lignite ay be directly correlated with its sodium content (1, 2). Consequently, oiler operators prefer to use lignite with a maximum of approximately weight percent sodium oxide in the ash for lignite of approximately percent ash. Obtaining such lignite is complicated by variation in odium content both from mine to mine and even within a specific mine (1).

Possible methods of reducing the effects of excess sodium in lignite nclude blending a low sodium lignite with a lignite containing a high odium content (1), providing additives to mask the effect of sodium 2), and physical or chemical removal of the sodium prior to burning (1, 3).

This work is part of a study being done to determine the feasibility f removing sodium from lignite by treating the lignite with an aqueous alt solution which effects the removal of sodium by cation exchange. An queous solution of calcium chloride was used in this investigation. pecifically, this work is concerned with investigating factors which affect he rate and extent of sodium removal. The variables studied were stirring ate of the lignite slurry, initial calcium chloride concentration in he liquid phase, particle size of the lignite, and moisture content of he lignite.

BACKGROUND

The first published reports of ion exchange phenomena were made by S. Thompson in 1850. He noted that ammonium sulfate absorbed by il could not be subsequently removed with water and that most of the monium sulfate was converted to calcium sulfate (4).

Since that time research has led to a better understanding of ion change on a molecular level. This, in turn, has allowed improvements the process and the exchange resin so that ion exchange is now nsidered a unit process. An ion exchange resin is considered "... as homogenous gel throughout which is distributed a network of hydrocarbon ains" (5), which contain ionic groups. These groups are immobile, their arge being balanced by other more mobile ions. An exchange resin provides source of mobile ions which, being only loosely held, may exchange with her ions in solution.

It has been shown that sodium is not present in lignite as separable mineral matter but probably is attached to the coal molecule itself (2). Whe contacted with an aqueous solution containing acid or a metal ion, lignite will exchange some or all of its sodium and other metals depending on experimental conditions (3). Since sodium is one of the easiest of the metal ions in lignite to remove in this manner, ion exchange represents a possible solution to the problem of reducing the sodium content of lignite.

Various methods which have been used to study ion exchange are:

1. Timed Samples.

This is the simplest method and consists of placing measured amoun of resin and a solution containing an exchanging ion into bottles and shaking the bottles. After measured periods of time the exchange is stopped and the liquid and/or resin analyzed (6).

2. Stirred Contactor.

Resin and exchange solution are combined and kept well agitated to insure good contact between the two phases. At timed intervals liquid samples may be withdrawn and analyzed (7, 8).

3. Shallow Bed Technique.

This type of rate determination apparatus employs a very shallow bed of resin through which the exchange solution is passed. If the concentration change in the liquid stream is small, data interpretation is aided since the material balance simplifies to an ordinary differential equation (9, 10). A small concentration change is required necessitating either a small sample or a large quantity of exchange solution.

4. Deep Bed Data.

The most difficult type of experimental rate determination to analyze involves passing an exchanging solution through a deep bed. Unless simplifying assumptions concerning the rate controlling step can be made, the mathematics can become unwieldy making interpretation of experimental data difficult (4).

5. Interruption Test.

This test provides a simple method for determining large concentration gradients within the solid phase. Provided such a gradient exists, interrupting a rate determination test by separating the phases should allow the gradient to relax. Resumption of the test after the gradient has relaxed should cause an increase in the rate of ion exchange. Of course, if a concentration gradient did not exist in the solid phase initially no rate increase would be noted (4, 8).

t was decided that a modified stirred contactor similar to that used by ressman and Kitchener (8) would provide a reliable technique for etermining the rate of ion exchange.

The stirring apparatus used in this study is shown in Figure 1. he device provides separation of the two phases permitting an interruption est to be made if desired. It permits the liquid phase to pass through the ignite sample continuously insuring intimate contact between the phases. urther, the rotation of the solids-containing stirrer keeps the liquid hase well mixed preventing concentration gradients in the bulk liquid hase. The phase separation also makes pipet sampling and analysis of the iquid phase easier. The device has an advantage over the shallow-bed echnique in that it does not require an extremely small sample nor a large mount of solution for use.

The stirring apparatus was suspended in the exchanging solution ontained in a covered, five-quart, baffled tank. The shaft was onnected to a Fischer variable speed stirrer. The variable speed stirrer as instrumented with a Metron hand tachometer, permitting constant bservation of the rotation speed of the stirrer. The motor was air-cooled uring operation. A schematic diagram is shown in Figure 2.

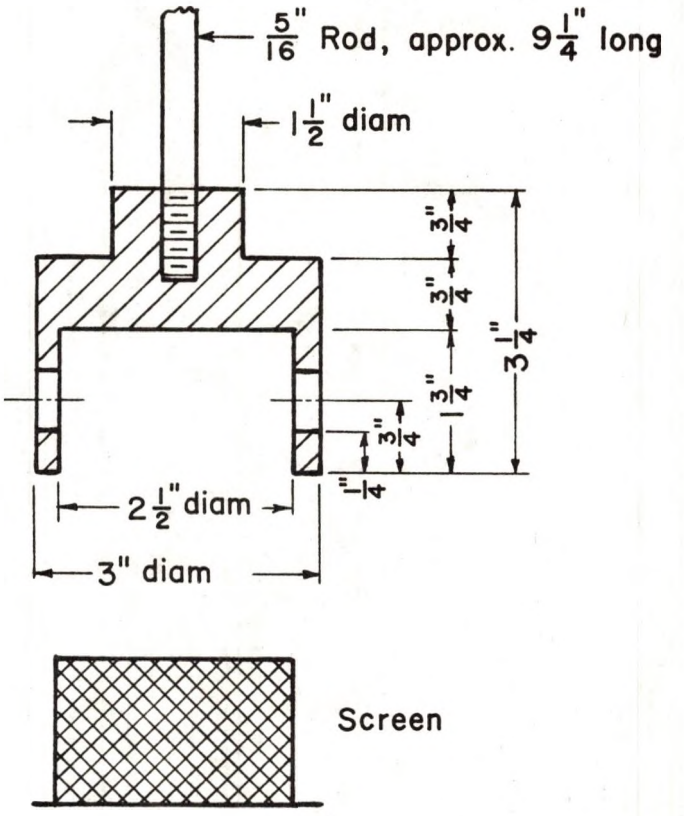
Since lignite is a porous structure (11), exchanging ions are carried rough capillaries until they reach some point where they react by exchanging th sodium. The freed sodium must diffuse back through the capillaries d out of the lignite particle. This sequence of events is similar to at found in the analysis of reactions in porous catalysts. Because of is similarity the hypothetical steps postulated for catalysis will be nsidered as descriptive of ion exchange also.

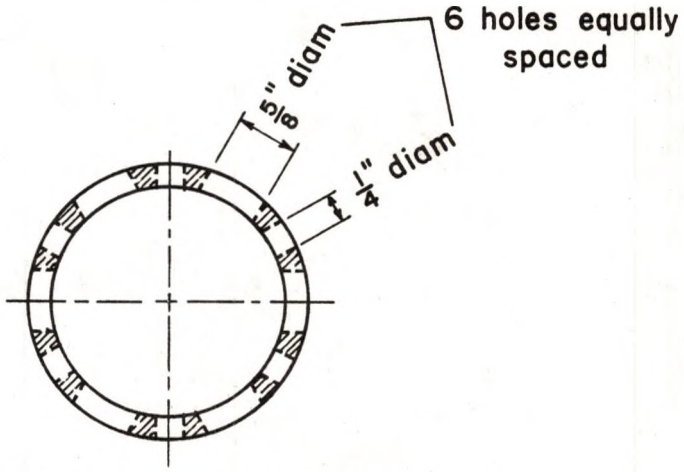
Authors differ on the number of steps to be considered to describe talysis but Aris (12) cites seven. They are as follows:

1. Diffusion of reactant from the bulk fluid phase, through a boundary layer, to the surface of the particle.
2. Diffusion of reactant into the solid through capillaries.
3. Adsorption of reactant at an active site.
4. Reaction at the solid surface.
5. Desorption of product.
6. Diffusion of product back through the pores to the exterior of the particle.
7. Diffusion of product through the boundary layer into the bulk fluid phase.

If the exchanging ions in solution are considered to be reactants d the sodium which was removed from the lignite as the product, these ps describe ion exchange.

The rate of ion exchange, as the rate of a catalyzed reaction, is sum of the rates for each of the hypothetical steps. However, in both exchange and catalysis, the data required to evaluate all of these





BOTTOM VIEW OF STIRRER

Fig. 1 Stirring apparatus for ion exchange experiment.

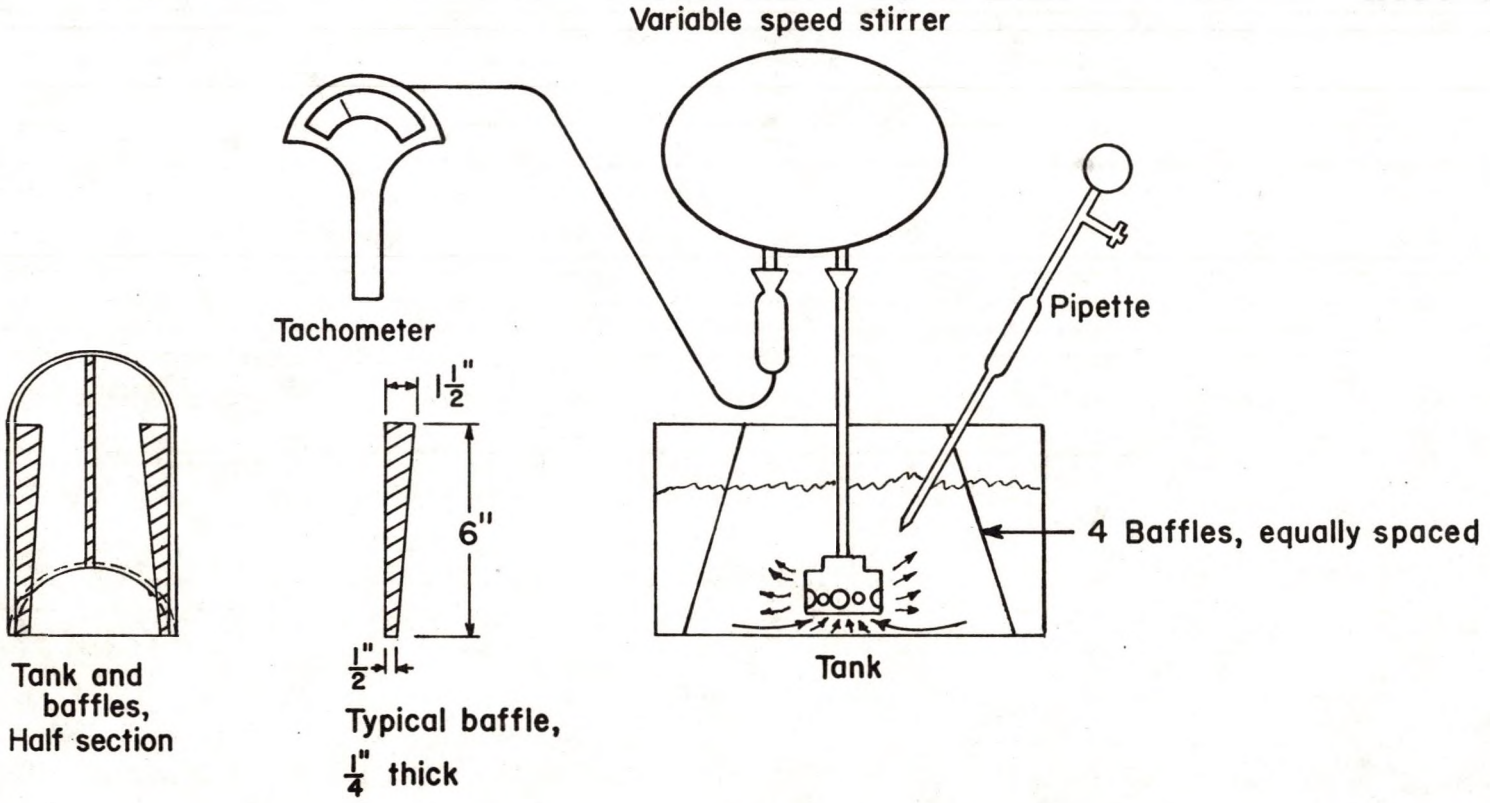


Fig. 2 Schematic diagram of experiment.

ates usually cannot be obtained. Consequently, it is necessary to assume hat only one step or a pair of steps control the rate. The other steps re assumed to be at equilibrium.

MATERIALS TESTED

Lignite from the North Beulah mine in Mercer County, North Dakota, as used for all tests. The proximate analysis and ash analysis on an s-received basis are given in Tables 1 and 2, respectively.

TABLE 1

PROXIMATE ANALYSIS OF BEULAH LIGNITE, PERCENT

	Moisture	Volatile Matter	Fixed Carbon	Ash
eulah lignite	35.58	26.24	30.62	7.56

TABLE 2

ASH ANALYSIS OF BEULAH LIGNITE, PERCENT

Loss on ignition at 800° C	0.6
Silica, SiO_2	20.6
Aluminum oxide, Al_2O_3	11.5
Ferric oxide, Fe_2O_3	11.4
Titanium oxide, TiO_2	0.5
Phosphorus pentoxide, P_2O_5	0.7
Calcium oxide, CaO	19.7
Magnesium oxide, MgO	7.1
Sodium oxide, Na_2O	7.1
Potassium oxide, K_2O	0.3
Sulfur trioxide, SO_3	20.8
Total	100.3

The lignite was crushed and screened to obtain three different size fractions. By Tyler screen size, the fractions were of 20 x 40 mesh, 10 x 20 mesh, and 6 x 10 mesh in size. Average particle size was determined by screen analysis. Three different moisture content lignites were obtained by air drying the lignite.

Unless otherwise noted, the exchanging solution was reagent grade calcium chloride dissolved in distilled water. Calcium chloride was chosen because it is highly ionized in solution. Owens has shown that when the calcium salt used in the exchanging solution was calcium oxide, the uptake of calcium by the lignite was greatly in excess of that required for ion exchange. He concluded that there was significant adsorption of the metal oxide by the lignite (13).

By choosing a salt which is highly ionized in solution, it was anticipated that adsorption of neutral species onto the lignite could be reduced or eliminated. The high solubility of calcium chloride in water also permitted concentrated solutions to be prepared to study concentr effects on the rate and extent of ion exchange. This is not possible with many of the other calcium salts because of their low solubility.

EXPERIMENTAL PROCEDURES

Solid samples for chemical analysis or for experimental runs were split from larger samples by hand riffling.

A solid sample for an experimental run was approximately 40 grams in si The sample occupied most of the volume of the screen basket yet permitted good mixing to take place.

In making a run a sample of lignite was weighed out on an analytical balance, then soaked for one hour in a covered beaker containing 100 millil of distilled water. This presoak was conducted for two reasons. First, if dry lignite were placed in the screen basket and immersed in the calciu solution, the lignite particles would not wet, thus preventing good contact between the phases. Second, other experimenters, working with synthetic resins, have found the rate of exchange to be low and erratic if the resins were not presoaked (6). Since presoak removed some of the sodium from the lignite, it is recommended that in the future the presoak period be shorter thus minimizing sodium loss during this step.

Near the end of the presoak period 3 liters of a previously prepared calcium chloride solution were measured out and placed in the baffled tank.

After the presoak was completed the liquid was drained from the solid, he solids placed in the screen basket, the basket inserted into the tirring apparatus, suspended in the calcium chloride solution (a stopwatch as started), and the stirrer was started. This procedure usually required 0 to 30 seconds.

The tachometer was observed frequently during the run and any eviation from the desired speed corrected.

Fifteen milliliter samples were withdrawn from the liquid at time qual to 3, 5, 15, 30, 60, and 120 minutes after initial contact of he solid with the calcium solution. Samples were also taken of the resoak solution and of the initial calcium chloride solution.

After the last sample was taken the motor was shut off, the stirring pparatus disconnected from the motor, and the stirrer removed from the alcium solution. The screen basket containing lignite was detached from he stirrer and suspended over a beaker to air dry for a minimum of 24 hours. fter drying, the lignite was leached with an acid-ethanol solution to emove the sodium and calcium. The leaching solution, approximately 25 percent thanol by volume, and 1 N. hydrochloric acid, removed essentially all odium and calcium from the lignite. Leaching permitted rapid analysis f the solid phase since it eliminated the usual ashing procedure. he leached lignite was stored temporarily for possible analysis should the aterial balance for the run not close.

Liquid samples were analyzed for sodium and calcium content. Sodium as determined using a Coleman Model 21 Flame Photometer; calcium oxide chelatometric titration using EDTA and screened indicators (14).

Duplicate runs were made and the results averaged.

DISCUSSION OF RESULTS

Rotation Speed

The experiments performed to determine the effect of rotation speed re made with lignite having an average particle size of 0.0245 inch 0 x 40 Tyler mesh), a moisture content of 15 percent (except for the 0 revolutions per minute [rpm] rerun), and an initial calcium chloride ncentration of 1,200 parts per million (ppm) (as calcium oxide).

Figure 3 shows that within the range of 200 to 600 rpm there seems to be little change in the rate or extent of sodium removal.

The results, with the exception of the 400 rpm rerun, indicate very little effect of rotation speed. The experiments for the 400 rpm rerun were made under the same conditions as the others except that the lignite contained 2.3 percent less moisture. Consequently, the lignite may have been weaker allowing more size degradation than usual during the run. If excess size degradation did occur, it would explain the slightly higher rate and extent of sodium removal since the surface area for reaction would be increased.

Since the results are somewhat inconclusive and since previous researchers using similar apparatus have found rotation speed to be an important factor in their studies (8), a second series of experiments was performed.

The second series of experiments were made with a larger particle size (0.0490 inches diameter, 10 x 20 Tyler mesh) and a lower initial calcium chloride concentration (160 ppm as calcium oxide) in an attempt to emphasize any effect due to rotation speed. The results are shown in Figure 4. It appears that 400 rpm may be slightly better than the other speeds; however, previous researchers (8) have shown that increasing agitation increased the rate of ion exchange continuously until a plateau was reached. Since no trend is evident in this work, it is felt that withi the 200 to 600 rpm range there is no optimum rotation speed for this proces

For comparison, and as a limiting case, tests were run under the same conditions but at zero rpm. These runs were made exactly as any other except that the motor was only turned on for a few seconds just before a liquid sample was withdrawn. The brief mixing insured that no concentrat gradients existed in the liquid and thus assured a true sample. As the graph shows, the rate and extent of sodium removal were lower at zero rpm.

Speeds between zero and 200 rpm and above 600 rpm were not tested because of equipment limitations.

It was concluded that rotation speed had little effect within the 200 to 600 rpm range but that some degree of agitation is required.

Initial Calcium Concentration

To observe the effect of various calcium chloride concentrations tests were made within a 0 to 1,250 ppm calcium chloride (as calcium oxide range.

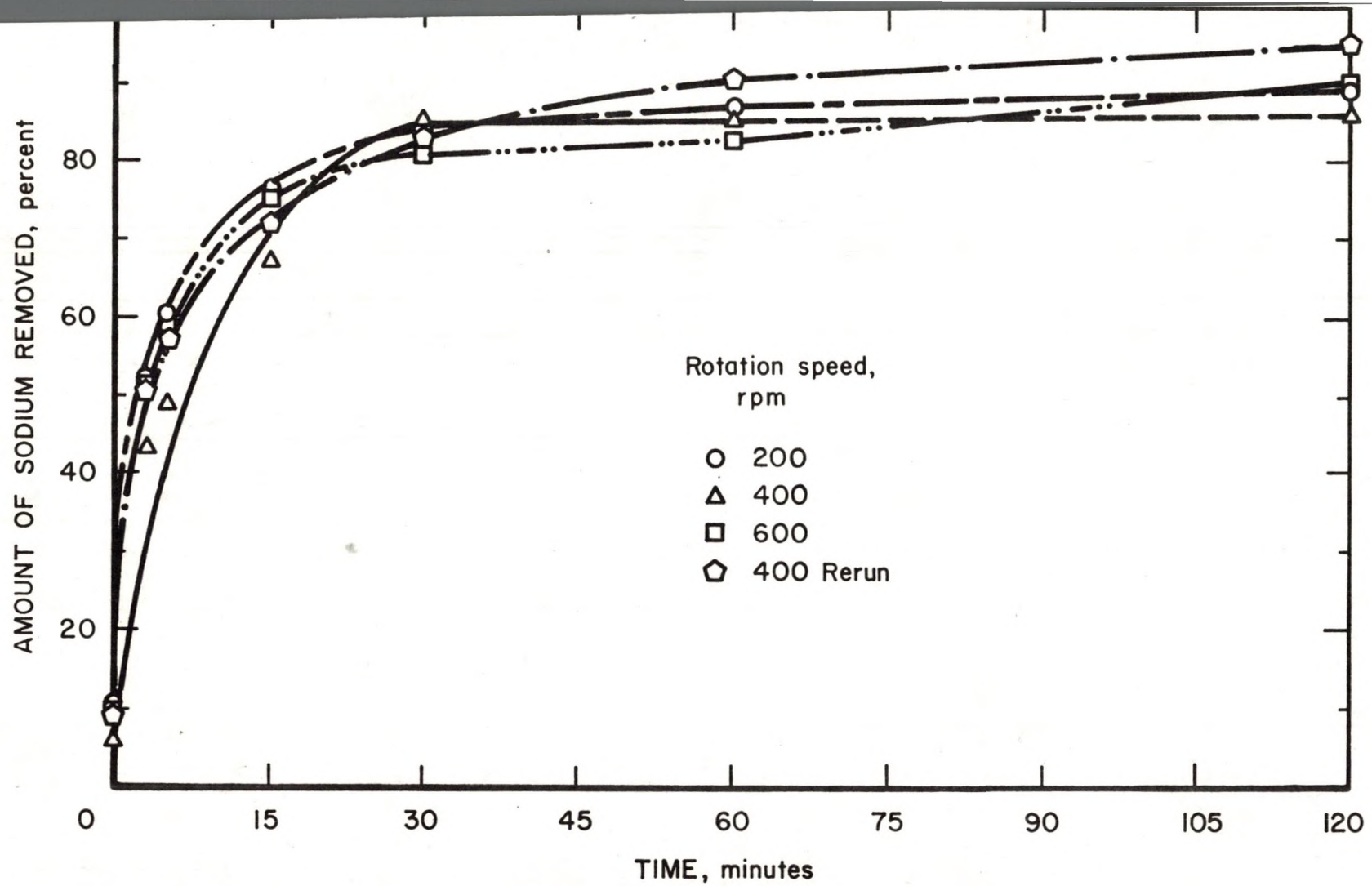


Fig. 3 Influence of rotation speed - average particle size, 0.0245 inches.

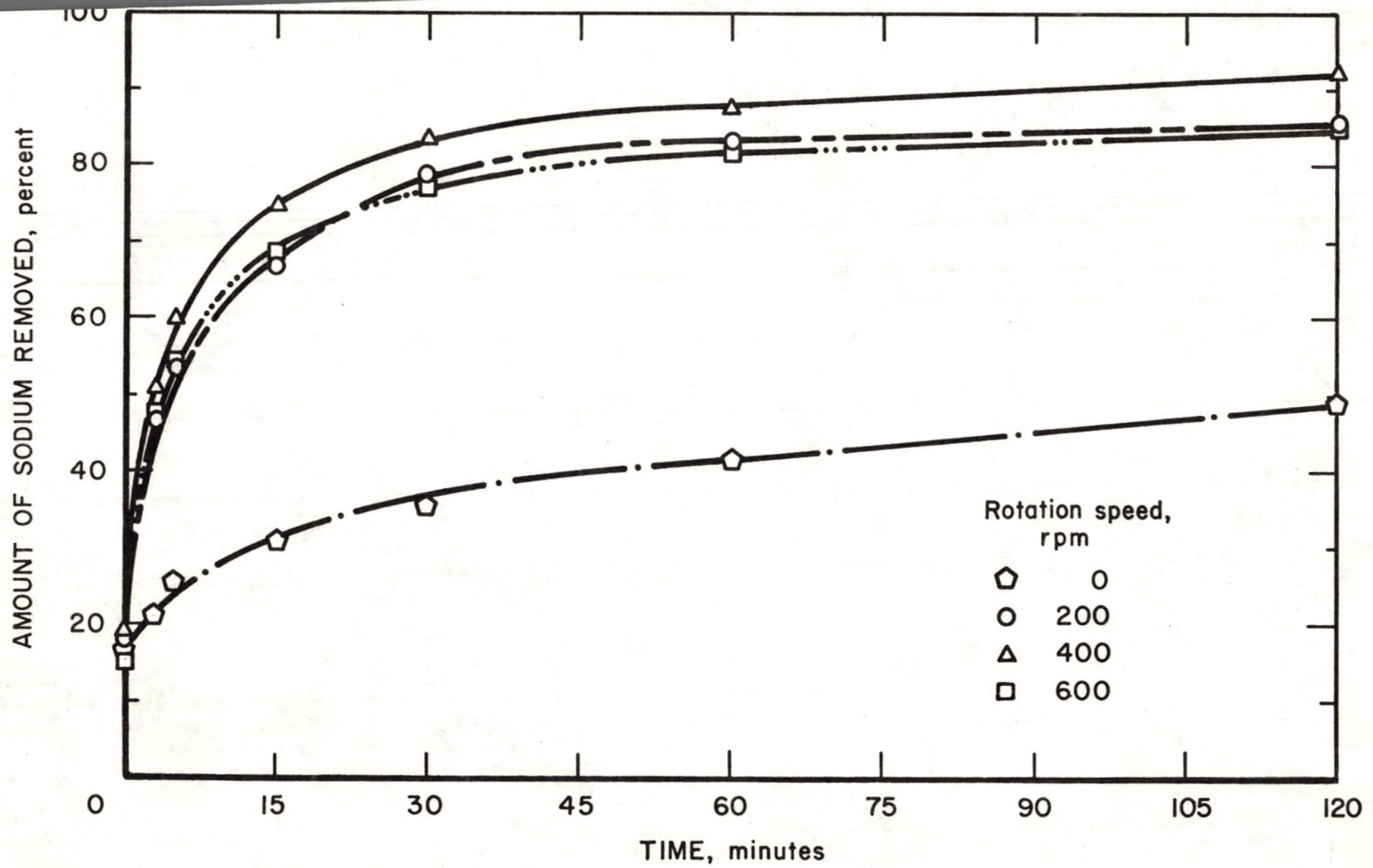


Fig. 4 Influence of rotation speed - average particle size, 0.0490 inches.

Since a greater calcium concentration would normally provide a greater driving force for the exchange, a relatively high calcium concentration would be expected to yield the greatest extent of sodium removal.

Figure 5 shows the results of tests made at 0, 400, 600, and 1,250 ppm calcium chloride (as calcium oxide). The runs were made using lignite with an average particle size of 0.0492 inch (10 x 20 Tyler mesh) and rotated at 400 rpm. The moisture content of the lignite was 15.4 percent in all cases except the zero ppm runs.

The close grouping of the runs at 400, 600, and 1,250 ppm indicates no effect on rate or extent of sodium removal within that concentration range. This indicates that the rate controlling step for ion exchange within the 400 to 1,250 ppm calcium chloride (as calcium oxide) range depends on something other than the calcium concentration in the bulk liquid. An increase in the calcium chloride concentration, therefore, has little or no effect on the overall rate. Further evidence that this is true will be presented in the discussion of the stoichiometry of sodium-calcium exchange.

Two runs were made with distilled water rather than calcium chloride solution. The results are also in Figure 5. The lignite used in these tests had a moisture content approximately 5 percent higher than that used in the previous runs. As will be shown and discussed in the next section, this should have produced a higher rate than would be found had the moisture content been the same as the moisture content in the other runs. After 2 hours the distilled water had removed 29.4 percent of the sodium initially present in the lignite. More than half of that had been removed in the presoak prior to the run. Recalling that 29.4 percent sodium removal is a generous figure due to the influence of moisture content, it is noted that the rate and extent of sodium removal with distilled water is quite low. Further, since 50 percent more sodium is removed with the higher calcium concentrations after two hours than with distilled water, the rate of sodium removal by ion exchange is much higher than the rate of sodium diffusion into distilled water.

Experiments have been conducted at initial calcium chloride concentrations between zero and 400 ppm (as calcium oxide) but the moisture content of the lignite was not the same as in this case. Therefore, the results cannot be compared. However, the runs do indicate that as the calcium concentration in the liquid is reduced the exchange becomes more "efficient" (consumes less calcium per unit of sodium removed). Thus, although no influence in the rate of exchange is discernable within the 400 to 1,250 ppm calcium chloride (as calcium oxide) range, at some point below 00 ppm there is an increase in the number of moles of sodium removed from lignite per mole of calcium removed from solution.

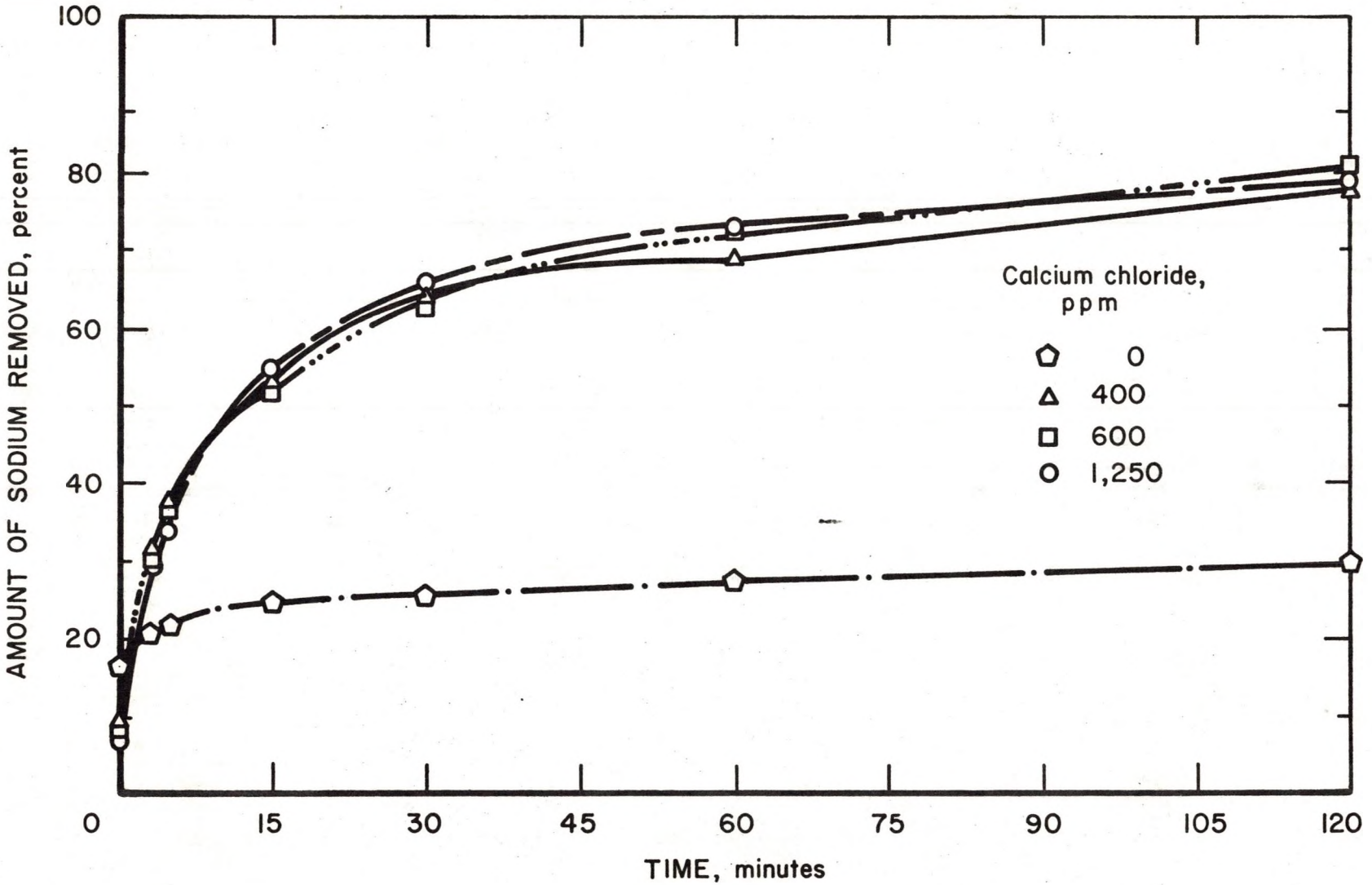


Fig. 5 Effect of initial calcium chloride concentration.

Moisture Content

If Figures 3 and 4 are compared it will be noted that the curves differ only slightly. This is unexpected since the average particle size for the runs represented in Figure 4 is approximately twice that of those in Figure 3. It may be understood, however, once the effect of moisture content on the rate and extent of sodium removal is noted.

Figure 6 shows the effect of varying the moisture content of the lignite. The moisture content given is the moisture content of the lignite before presoak.

Comparing the 15.5 and 19.9 percent moisture content curves of Figure 6, it will be noted that a 4.5 percent change in moisture content produced more than a 10 percent increase in the extent of sodium removal at the end of 2 hours. The initial rate for the higher moisture content lignite is also greater. After approximately 20 minutes, however, the rate of the 15.5 percent moisture content lignite curve becomes greater than that of the higher moisture lignite. This may readily be seen by noting that at time equal 20 minutes the difference between the curves is nearly 25 percentage points while at 2 hours it has decreased to 10 percentage points.

In an attempt to discover whether even greater moisture content will cause a higher rate and extent of sodium removal, lignite with a moisture content of 33.2 percent was tested. As the graph shows, this 13.3 percent increase in moisture content produced less than a 2.5 percent increase in the extent of sodium removal after 2 hours.

This suggests that below approximately 20 percent moisture content in lignite, the extent of sodium removal is relatively low. In a commercial process then, any drying of lignite below 20 percent moisture should take place after the lignite has been treated by ion exchange. Freshly mined lignite, however, should not require any special treatment to prevent drying since it should not air dry below 20 percent moisture.

To explain the marked influence of moisture content on the rate of exchange it is helpful to recall that lignite has a porous structure. Data to support the existence of such a structure and the distribution of capillary sizes in lignite have been gathered by previous researchers (11). Their work also postulates that as lignite dries uneven shrinkage of the lignite particle occurs causing degradation. This degradation could be either gross, in which the particle disintegrates, or subtle, causing only the closing of some of the capillaries. In the latter case, once lignite capillaries have been closed rewetting of the lignite will not cause all of them to reopen. The diffusion of calcium into the lignite particle and sodium out of the particle through the capillaries is thus hampered. It is, therefore, concluded that reducing the moisture content of lignite below approximately 20 percent causes sufficient permanent capillary loss to seriously affect the rate and extent of ion exchange.

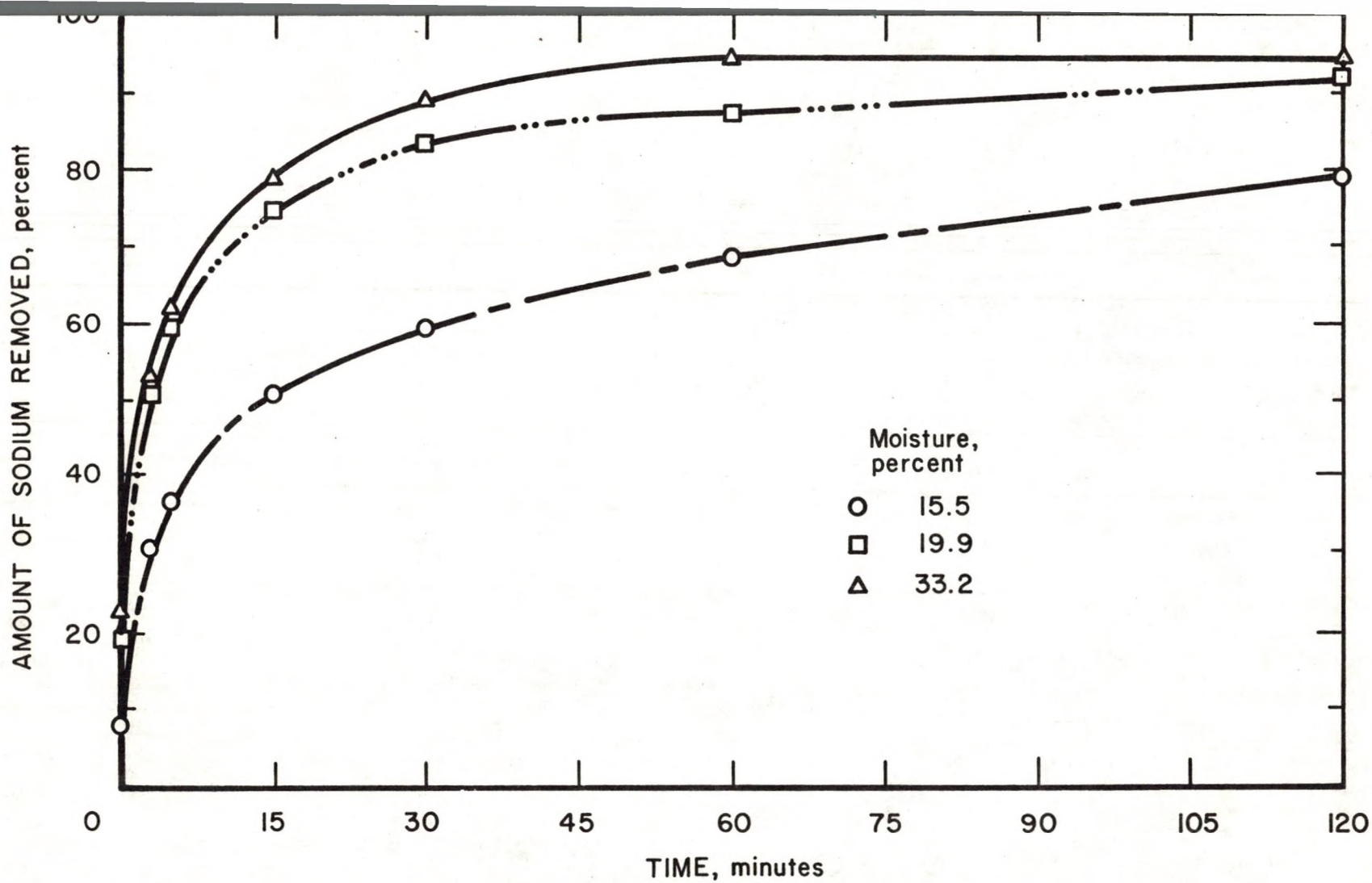


Fig. 6 Effect of moisture content of the lignite.

Particle Size

Although differences in the moisture content of the lignite have been shown to cause two different sizes of lignite to act as though they were nearly the same, particle size influences should not be neglected. Figure 7 shows the results of experiments performed to observe the influence of particle size on the rate and extent of sodium removal.

The upper curve has an average particle size of 0.0490 inch (10 x 20 Tyler mesh); the lower a size of 0.0962 inch (6 x 10 Tyler mesh). Figure 7 shows the smaller particle size has a higher rate of exchange initially and a greater extent of sodium removed at the end of 2 hours. Although the larger particle size has a lower rate of exchange initially, after 15 minutes its rate becomes greater than that of the smaller size. As in the case of moisture content, this can be seen by noting the magnitude of the difference between the curves at time 15 minutes compared to that after 2 hours.

Using the porous model of lignite, the influence of particle size is easily explained. As the size of a particle under consideration is increased the complexity and length of any capillary paths leading to its interior would also increase. Thus as the tortuosity of the path increases, the time required for calcium solution to reach the interior regions of the particles and for exchanged sodium to diffuse out of the particle are both increased. This would explain the greater extent of sodium removal for the smaller particle size lignite as observed in Figure 7. The curves are becoming closer after two hours, however, which suggests that the larger particle size lignite may not as yet have reached equilibrium. Future studies may show that equilibrium conditions may not be the most economical so the importance of equilibrium is uncertain.

It is concluded that although the effect of the moisture content of lignite can overshadow the influence of its particle size with regard to the rate of ion exchange, normally as particle size is increased the extent of exchange decreases.

The Stoichiometry of Sodium-Calcium Exchange

Ideally the exchange of sodium for calcium would occur at the stoichiometric ratio of two sodium ions per calcium ion. The exchange probably does take place in a 2 to 1 ratio but other conditions and side reactions affect the calcium uptake of the lignite.

The calcium chloride solutions used in this work normally yielded a reasonable "exchange ratio" (moles of calcium oxide removed from solution per mole of sodium appearing in solution). The exchange ratio was, however, in all cases above the theoretical value of 0.5.

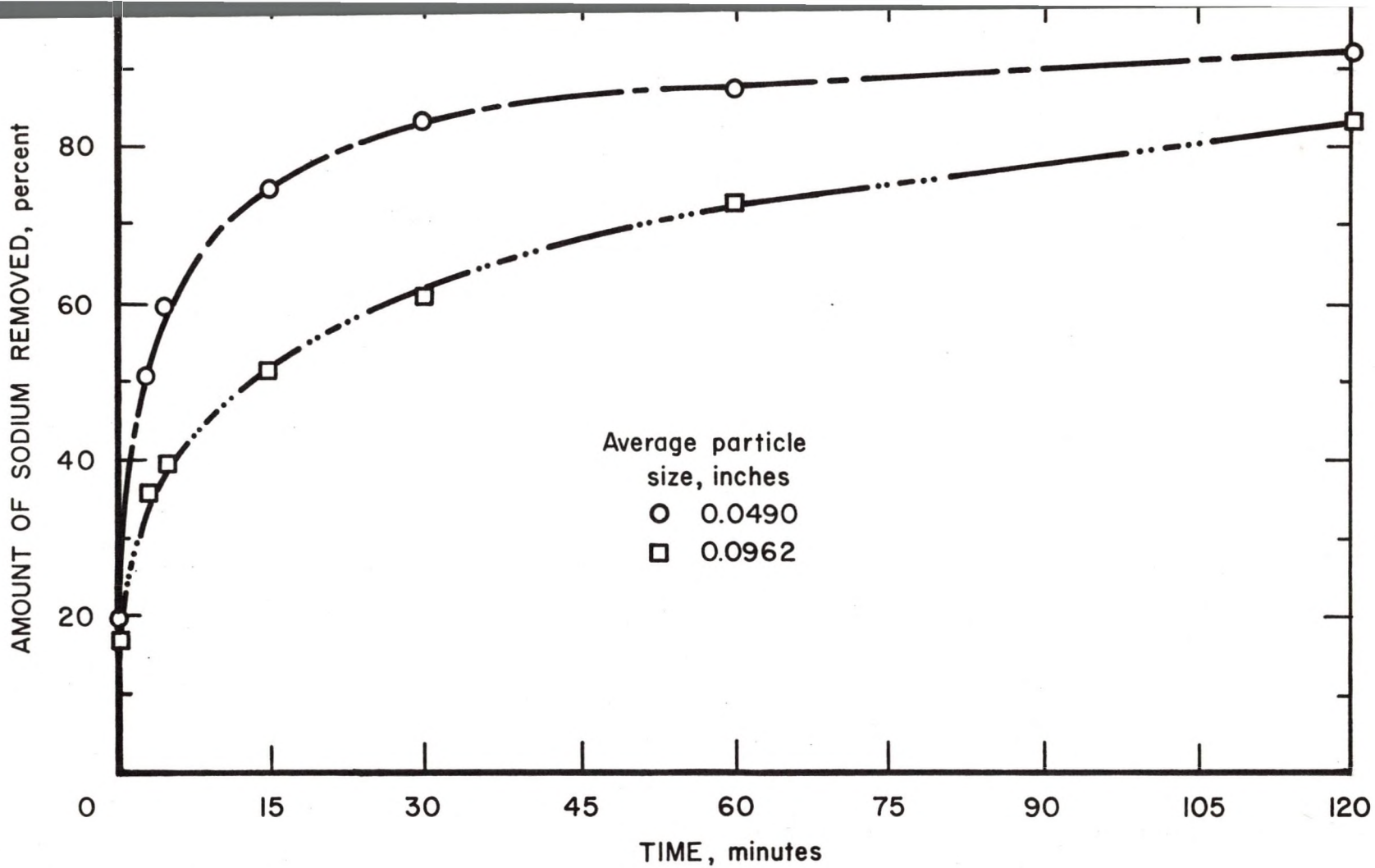


Fig. 7 Effect of particle size of the lignite.

Figure 8 shows the results of all tests. The ordinate of the graph is the "exchange ratio". This should tend to 0.5 if calcium was used only to exchange with sodium. The ordinate may be considered a measure of the "efficiency" of the reaction with 0.5 considered to be 100 percent "efficiency." The abscissa plots the number of moles of calcium oxide in solution prior to exchange per mole of sodium in the lignite before any exchange. The abscissa could be considered a measure of excess calcium to sodium or as a "driving force" for the exchange.

For an average particle size of approximately 0.0245 inches (20 x 40 Tyler mesh) the plot is nearly horizontal at an "exchange ratio" of 1.1 above a "driving force" ratio of nine. Below nine the curve slopes downward to higher "efficiency," reaching an "exchange ratio" of 0.64 at a "driving force" of 1.27. The larger particle size (0.0491 inches - 10 x 20 Tyler mesh) curve also tends toward higher "efficiency" as the "driving force" is decreased. Two determinations were made with 0.0962 inches (6 x 10 Tyler mesh) average particle size lignite. The position of the points from those experiments on the graph also indicates that as the "driving force" is decreased toward unity the exchange becomes more "efficient."

To understand why the overall ion exchange never assumed stoichiometric proportions two facts must be considered. First, lignite contains exchangable ions other than sodium, as may be seen from the ash analysis. The order of ease of replacement of such ionic cations is normally $H^{+}>Na^{+}>K^{+}>Mg^{++}>Ca^{++}>Al^{+++}>Fe^{+++}$ (4). Thus, calcium should easily replace ionic hydrogen, potassium, and magnesium besides sodium. Further, as the calcium concentration in the liquid phase increases, aluminum and iron may be replaced in an attempt to establish equilibrium between solid and liquid phases. In the horizontal portion of the curves in Figure 8 this is probably what is occurring. All the sodium that can exchange has done so and remaining excess calcium in the liquid is maintaining equilibrium by exchanging with aluminum and iron. Exchange with ions other than sodium may be considered side reactions for this system. As such they are, for the most part, undesirable since they move the exchange away from the theoretical 0.5 "exchange ratio" by using calcium for purposes other than for the exchange of sodium.

The horizontal portion of the curves may also represent an irreducible level of sodium in a given size of lignite. Thus Figure 8 would show that the smallest particle size lignite gives up more of its sodium than either of the larger sizes.

A second cause for a higher "exchange ratio" is that lignite may adsorb neutral species from solution. This has been observed by Owens in his work with calcium oxide (13). Such adsorption would increase the amount of calcium used per sodium obtained and consequently increase the "exchange ratio." It is suspected that a combination of side reactions and adsorption explain why the "exchange ratio" fails to reach its theoretical value. Which one of the two, side reaction or adsorption, is more important is probably a function of the salt used for ion exchange and its concentration in solution.

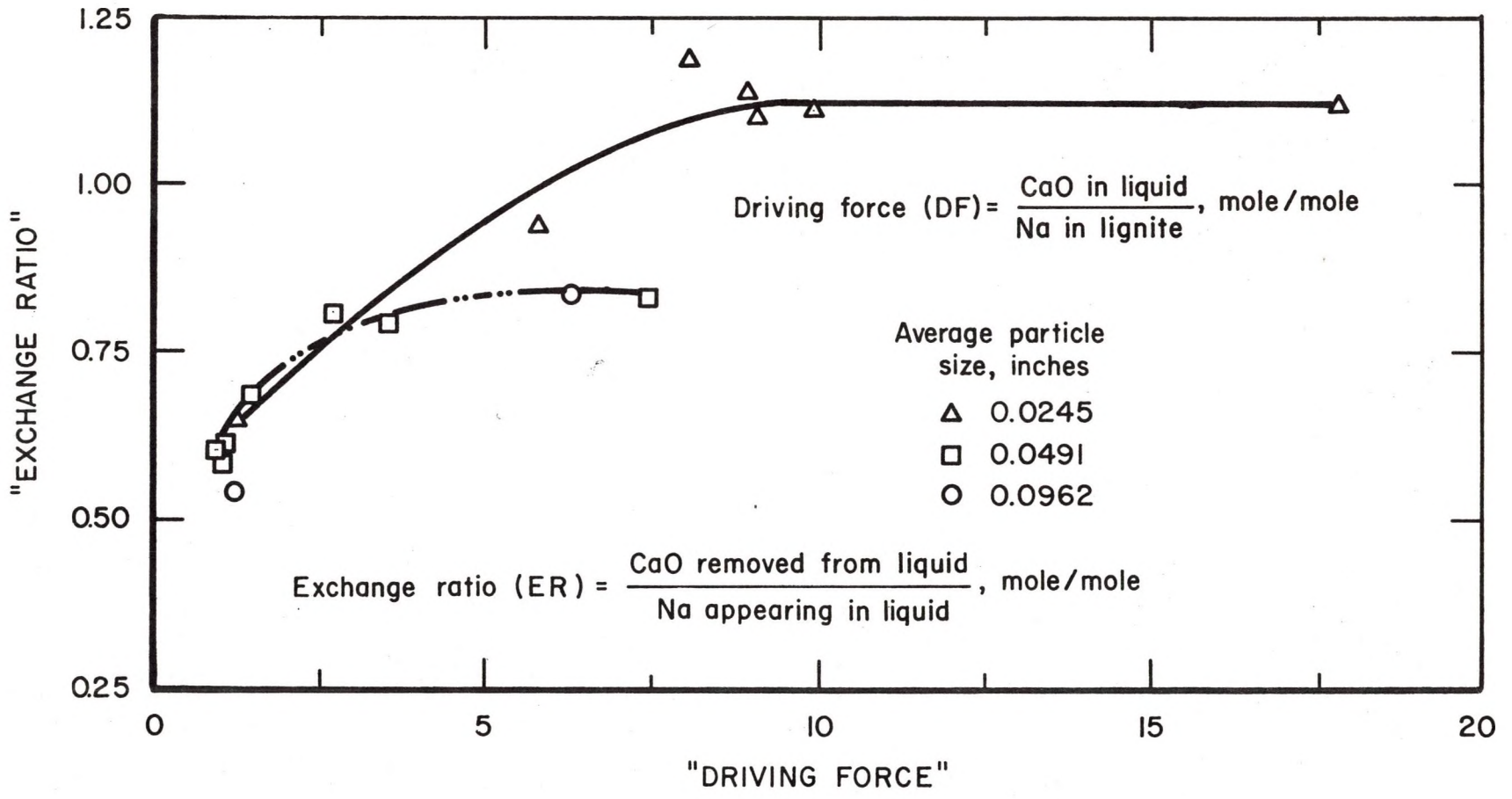


Fig. 8 Variation of "exchange ratio" with " driving force".

Since calcium chloride is highly ionized in solution, at low concentrations the probability of occurrence of a neutral species suitable for adsorption is low, therefore, adsorption would be unimportant. At higher calcium chloride concentrations, or with a less highly ionized salt, the probability of finding a neutral species would increase and so too would the importance of adsorption.

It is concluded that if only sodium is to be removed from lignite, solutions containing one mole of calcium chloride per mole of sodium in the lignite are preferable to solutions having higher calcium content.

CONCLUSIONS

The following conclusions were drawn from this study.

(1) With the exception of zero rpm and within the range of speeds tested the rate of stirring had no effect on the rate of ion exchange.

(2) Calcium chloride is an effective agent for removing sodium from lignite by ion exchange.

(3) If the moisture content of the lignite falls below 20 percent the rate of ion exchange is slowed appreciably.

(4) As the average particle size of lignite increases the rate of exchange decreases.

(5) The stoichiometry of the exchange is such that as the ratio of calcium chloride available in the liquid to sodium available in the lignite decreases to 1.0 the exchange tends toward theoretical stoichiometric proportions.

(6) The observations made in this study are consistent with the porous model of lignite proposed by Lavine.

RECOMMENDATIONS

Some recommendations are:

(1) Other salts or acids should be used for ion exchange.

(2) Lower values of the "driving force" could be studied.

(3) Larger particle sizes should be studied.

(4) The influence of rotation speed could be studied outside the range used in this work.

(5) Interruption tests could be used to learn more about the mechanism of ion exchange.

(6) An attempt could be made to fit these data to a mathematical model for ion exchange.

(7) Lignite could be studied by other rate measuring techniques and the results compared with this study.

APPENDIX

TABLE 3

SUMMARY OF DATA[a]

Particle Size, Inches	Percent				Rotation Speed	$[CaCl_2]$[b]	Percent Sodium Removed In:[c]							"Exchange Ratio"	"Driving Force"	Material Balance	
	Ash	Moisture	Na_2O	CaO			Presoak	3	5	15	30	60	120			Na	CaO
0.0245	8.58	15.06	7.6	21.4	400	2,520	6.60	47.4	55.3	69.8	77.9	85.7	89.2	1.12	17.8	96.6	99.6
.0245	8.58	15.06	7.6	21.4	400	1,120	6.04	43.4	48.7	67.3	84.9	85.8	—	1.18	8.16	95.6	97.4
.0245	8.58	15.06	7.6	21.4	600	1,230	9.57	50.6	58.2	76.0	81.2	83.0	90.1	1.14	8.91	99.9	98.1
.0245	8.58	15.06	7.6	21.4	200	1,220	9.98	50.4	58.4	76.4	84.5	87.2	89.9	1.10	9.03	100.0	98.5
.0245	8.56	13.13	7.2	20.5	400	1,260	8.36	50.8	57.6	72.0	83.6	91.3	96.1	1.11	9.98	106.0	98.9
.0245	8.56	13.13	7.2	20.5	400	772	8.50	48.6	55.0	71.4	85.0	91.4	94.2	.94	5.77	109.0	99.8
.0245	8.56	13.13	7.2	20.5	400	162	9.74	50.6	57.4	72.6	84.0	91.6	94.4	.645	1.26	111.0	101.0
.0492	8.34	15.42	7.4	21.3	400	1,250	7.48	31.4	33.5	54.5	66.0	72.6	79.0	.826	7.42	100.0	94.6
.0492	8.34	15.42	7.4	21.3	400	592	9.31	31.2	37.1	52.4	63.4	72.2	81.0	.794	3.55	102.0	95.6
.0495	8.40	15.52	7.4	21.7	400	398	7.99	30.8	36.8	50.8	59.4	68.4	78.7	.803	2.70	101.0	92.2
.0490	8.31	19.87	7.4	21.4	400	0	16.3	20.5	21.2	24.3	25.4	27.4	29.4	0	0	102.0	91.2
.0490	8.31	19.87	7.4	21.4	400	163	19.2	50.4	59.8	74.4	83.6	87.4	92.0	.596	1.02	99.5	94.2
.0490	8.31	19.87	7.4	21.4	600	160	15.4	48.0	54.0	68.4	77.6	82.0	85.1	.616	.998	83.2	94.8
.0490	8.31	19.87	7.4	21.4	200	163	17.9	46.7	53.6	66.7	78.5	83.1	85.3	.612	1.02	93.4	94.8
.0490	8.31	19.87	7.4	21.4	0	162	17.1	21.3	25.8	30.9	35.8	41.9	49.4	.287	1.04	98.7	89.2
.0492	7.19	33.19	7.4	21.0	400	162	22.8	53.0	62.0	78.7	88.8	94.4	94.4	.687	1.49	98.9	94.2
.0962	7.44	18.68	7.9	20.4	400	162	16.7	35.9	38.6	51.4	60.6	72.8	83.4	.548	1.21	109.0	96.4
.0962	7.44	18.68	7.9	20.4	400	790	17.0	35.8	39.2	52.0	62.6	74.3	84.2	.832	6.26	106.0	96.3

[a] Results given are averages of duplicate runs.

[b] Concentration of calcium chloride as calcium oxide.

[c] Time in minutes.

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